EXPERIMENTAL INVESTIGATIONS OF LOW-ENERGY (4-40 eV) COLLISIONS OF O⁻(^{2}P) IONS AND O(^{3}P) ATOMS WITH SURFACES

A. Chutjian,* O. J. Orient* and E. Murad[+]

*Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109
[+]Air Force Geophysics Laboratory, Hanscom Air Force Base, MA 01731-5000

ABSTRACT

Using a newly-developed, magnetically confined source low-energy, ground state oxygen negative ions and neutral atoms are generated. The energy range is variable, and atom and neutrals have been generated at energies varying from 2 eV to 40 eV and higher. We find that the interaction of these low-energy species with a solid magnesium fluoride target leads to optical emissions in the (at least) visible and infrared regions of the spectrum. We will discuss briefly details of the photodetachment source. We will then present spectra of the neutral and ion "glows" in the wavelength range 250-850 nm (for O⁻) and 600-850 nm (for O), and discuss the variability of the emissions for incident energies between 4 and 40 eV.

1 INTRODUCTION

The problem of vehicle "glow" emission in low-earth orbit (LEO) has been documented in some detail over the past several years. [See Ref.1 for a recent review of missions and observations.] By way of summary, the optical emissions observed from the the Shuttle bay window are from Shuttle surfaces oriented in the "ram" direction (along the Shuttle velocity vector), and have been associated with interaction of 5 eV ground-state oxygen atoms with the various surface materials. The emission spectrum in LEO has been measured, at the 3.4 nm resolution level, and found to be continuous in the range 450-800 nm, with a broad maximum at about 680 nm. Higher resolution spectra in LEO, extending to shorter wavelengths, are not available and would clearly be helpful in revealing any latent band structure and in identifying the emitting species.

There is thus far no definite explanation for the glow process. However, various scenarios have been suggested to account for the glow, with the most promising being that of Swenson, et al [2] in which the emission has been proposed to arise from the NO_2 recombination continuum. The excited NO_2^* molecules are formed on the surface by successive surface-mediated reactions of N and O by the so-called Langmuir-Hinshelwood mechanism. Desorbed, excited NO_2^* molecules emit in the $\tilde{A}^2B_1 \to \tilde{X}^2A_1$ continuum. The lifetime of the $\tilde{A}$ state (which determines the spatial extent of the glow above the Shuttle skin), and the wavelengths of emission are both consistent with Shuttle observations.

Because of the difficulty in generating fast, ground-state atomic oxygen in the laboratory, simulation followed by a clear understanding of the mechanism for the surface glow has been a tedious process. Methods for generating oxygen atoms usually suffer from one or more of the following properties: the atoms are too slow – less than 1 eV in energy (plasma discharges); there is an unknown admixture of excited molecules and atoms (positive-ion charge exchange, or high-power laser sources that use either a solid target or a dense gaseous target); or peak pulsed O-atom fluxes are so high (order of 10^{20} atoms/cm²-sec for so-called "accelerated testing" by high-power pulsed laser sources) that one "burns plastic" rather than bathing the surface in an LEO-encountered flux of 10^{13}-10^{15} atoms/cm²-sec.

We present in Sec. 2 a description of the JPL atomic oxygen source which generates ground-state O-atoms of quantum state, energy, flux, and beam purity simulating that encountered in LEO. It has been used to obtain first spectra of the glow phenomenon in the laboratory. The MgF_2 surface chemiluminescence spectra using low-energy O^- ions is described in Sec. 3, and chemiluminescence spectra using low-energy O-atoms are given in Sec. 4.

2 OXYGEN-ATOM SOURCE DESCRIPTION

The JPL atomic oxygen source was designed specifically to study the mechanism of the spacecraft glow phenomenon, degradation of materials in LEO, and to carry out basic fast-atom collision studies with neutral gaseous targets. Techniques used in the source involve the following steps carried out in a uniform, high-intensity solenoidal magnetic field (see Fig. 1): (a) generate $O^-(^2P)$ ions via dissociative attachment to NO at 8 eV electron energy (point G); (b) accelerate the O^- ions and electrons to the desired final energy (5 eV, say); (c) by trochoidal deflection (T_1) separate the higher-velocity electrons from the slower O^- ions, and trap the electrons in their Faraday cup; (d) detach the electron from O^- by a cw laser and a multiple-pass mirror (M) geometry; and (e) direct the O^- and O beams toward the target, and reflect the undetached O^- beam by biasing the target negative with respect to the O^- kinetic energy. Alternatively, a second trochoidal deflector, located immediately after the mirrors M, was sometimes used to separate the ground-state $O(^3P)$ atoms from undetached O^- ions, and trap the latter in a separate Faraday cup for analysis of the O^- beam.

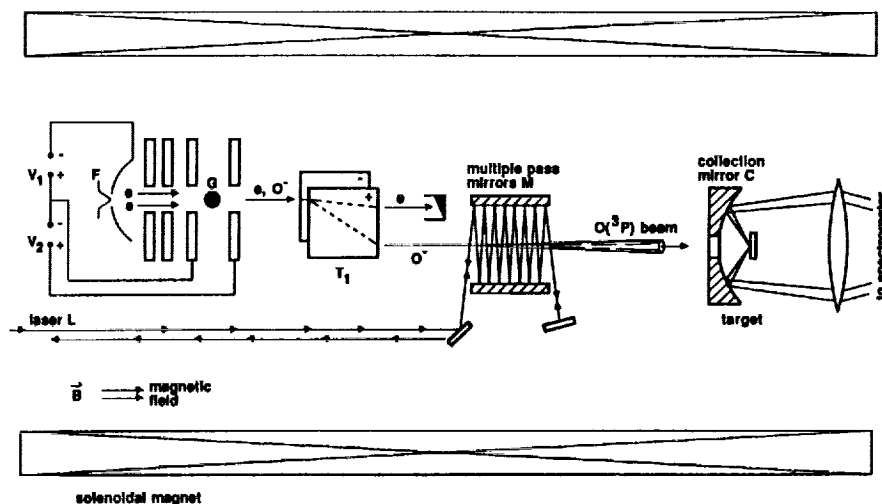The laser wavelengths are restricted to visible lines of an argon-ion laser so that

Figure 1. Schematic diagram of the magnetically-confined, photodetachment O-atom source.

detachment results exclusively in ground-state atoms [3]. For a 20 watt laser, 5 eV ions, and 100 passes across the confined ion beam, one obtains about a 15% detachment efficiency into $O(^3P)$. Furthermore, if wavelengths shorter than about 360 nm are used, one may also generate a mixture of $O(^1D)$ and $O(^3P)$ atoms. This capability is useful in studying differential reaction effects of electronically-excited atoms, such as O-atom addition to double-bonds in epoxies and organic molecules.

In order to minimize rapid divergence of the O-atom beam after detachment, care was taken in the source to restrict the energy of the O^- ions perpendicular to the B field. This involves choosing the target gas (at G) to provide small O^- kinetic energy at onset, and giving due regard to the space-charge repulsion between the ions, especially at high O^- currents.

For both the O^- and O-atom studies, the same sample of MgF_2 was used as the target. A 95% transmitting tungsten gauze covered the surface to prevent surface charging by the O^- beam; and also to allow repulsion of the O^- beam during the O-atom measurements. A large, high-reflectivity mirror at C (Fig. 1) was used to collect a broad spatial extent of optical emissions from the target. These emissions were focused onto the entrance plane of a fast f/3.5 double-grating monochromator capable (for the O-atom case) of attenuating by a factor 10^9 laser lines at 500 nm from spectral emissions at 600 nm. The detection system used an RCA phototube with a gallium arsenide photocathode and a manufacturer's stated long-wavelength cutoff of 900 nm. Fast, pulse-counting electronics were used, and spectra accumulated by multichannel scaling.

3   THE NEGATIVE ION [$O^-(^2P)$] GLOW

We show in Fig. 2 spectra of the $O^-(^2P)$ glow from a MgF_2 surface in the wavelength range 250-850 nm, and at four O^- energies ranging from 5-40 eV. The currents were in the range 1.0 -5.0 μa, or fluxes of (0.32 -1.6) $\times$ 10^{14} ions/cm^2-sec. The spectra in Fig. 2 were normalized to a common flux of 1.0 $\times$ 10^{14}. Care was taken in these measurements to prevent surface charging of the dielectric target by use of a transparent, conducting tungsten gauze on the target surface. This gauze itself was shown not to contribute to
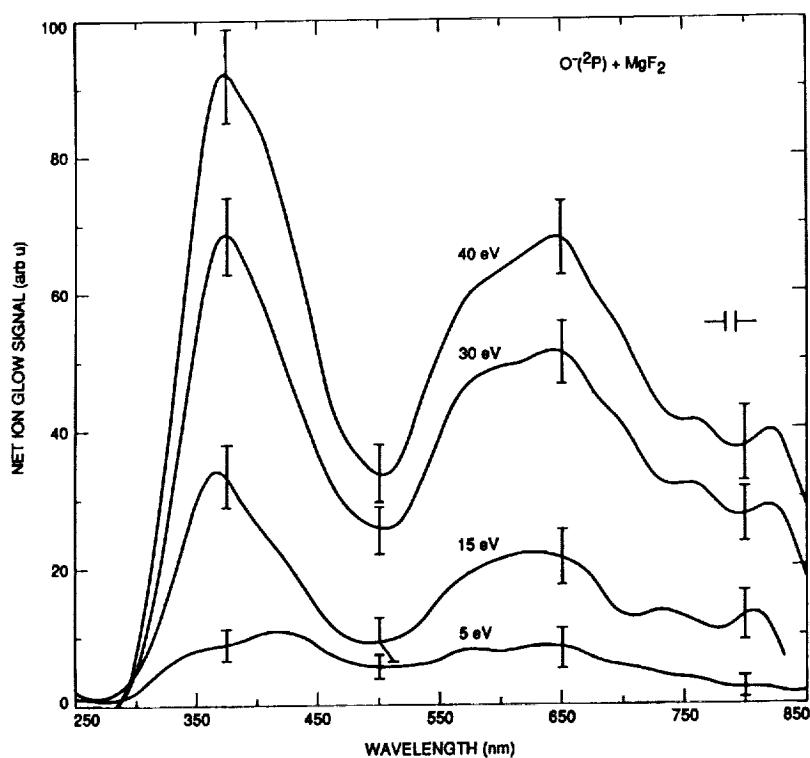

Figure 2. Glow signal of negative oxygen ions $O^-(^2P)$ from a MgF_2 surface, at the indicated O^- collision energies.

the observed spectra. Also, a glow contribution arising from interaction of the O^- beam with the background gas (mainly NO) was observed. This contribution to the spectrum was measured by taking spectra with the tungsten gauze biased negatively, so that the O^- beam was reflected just above the MgF_2 target.

One sees in Fig. 2 that the O^- glow from MgF_2 is characterized by two broad, unstructured (at the 10 nm resolution level of the present measurements) spectral emissions: one peaked near 375 nm, and the second at 600-650 nm. The spectral intensity is a strong function of O^- energy, with emission being strongest at 40 eV, and diminishing rapidly at energies near 5 eV. No attempts have been made to indentify the origin of these features pending experiments to be carried out under more controlled vacuum and surface conditions (see Sec. 4).

It is interesting to note that at high fluxes (order of 10^{14}), the O^- glow is easily visible to the eye, having a bluish appearance (not resembling, that is, the orangish Shuttle glow!).

4   THE ATOMIC OXYGEN [O(^{3}P)] GLOW

Shown in Fig. 3 are spectra in the wavelength range 600-850 nm arising from the interaction of 4, 5 and 40 eV O(^{3}P) oxygen atoms with the same MgF_2 surface. Comparison of these
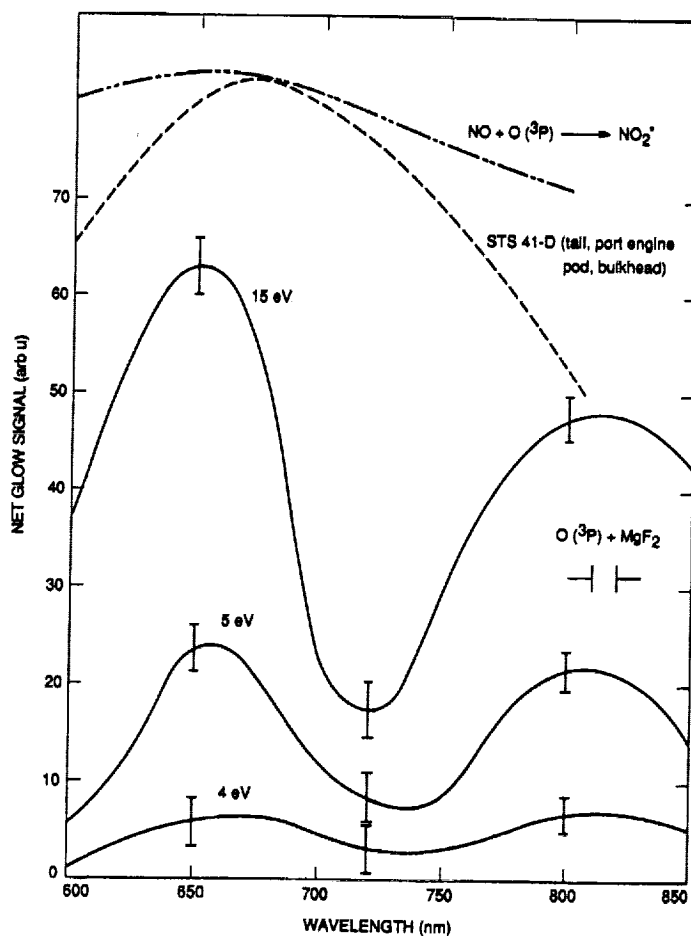

Figure 3. Glow signal of ground state atomic oxygen atoms O(^{3}P) from a MgF_2 surface, at the indicated O-atom collision energies.

spectra are made with glow results from the STS 41-D mission [2], and from laboratory-measured NO + O recombination spectra at thermal oxygen-atom energies [4,5].

The spectra in Fig. 3 were approximately two-to-three orders of magnitude weaker than the O^- glow spectra of Fig. 2. Reasons for this are (a) the efficiency of the photodetachment step is only about 10%, (b) the O-beam, no longer confined by the magnetic field, diverges as it travels toward the target from a combination of imparted kinetic energy in the dissociative attachment step, and effects of space-charge repulsion in the O^- beam, and (c) the conversion efficiency of O-atoms to visible photons is estimated to be quite low, about 2.5×10^{-6} [6].

As a result, a number of other background sources had to be identified and eliminated from these spectra. The major contributors were : (a) a persistent fluorescence signal B_L arising from the detachment mirrors with the laser on, (b) photons B_{O^-} arising from interaction of the O^- beam with the background gas, and (c) photons B_F from the electron-gun filament. The net glow signal G was obtained over four cycles of signal-gathering. These were (1) photon counts with laser on and O^- beam on, (2) counts with laser on and O^- off, (3) counts with laser off and O^- on, and (4) counts with laser off and O^- off. The net glow signal G was then given by (1) - (2) - (3) + (4). The error limits shown in Fig. 3 reflect the sum of the four statistical errors in the individual counting cycles.

Also considered in this sequence was the fact that the background B_{O^-} in steps (1) and (3) are not the same, due to depletion of O^- by detachment. We found that this depletion had to be about a factor of 2.5 greater than could be accounted for solely by detachment. The reason for this is not clear. It could lie either in the measured value [3] of the detachment cross section being a factor of 2.5 too low; or that the detachment cross section of O^- is enhanced (by the same factor) via Landau resonances of the detached electron in the solenoidal magnetic field. Calculations based on works of Crawford [7] and observations by Krause [8] show that these resonances do persist up to 1 eV above detachment threshold. Enhancement is thus possible in our case, given the homogeneity of magnetic field (estimated to be better than 0.5% in the detachment region), laser bandwidth (8 GHz), and spacing of the resonances (169 GHz, neglecting overlapping fine-structure transitions and Zeeman splittings).

One striking feature in Fig. 3 is that the glow is continuous (10 nm resolution level) and shows two prominent maxima, one at 650 nm and the second at 800-825 nm. The first maximum is in good agreement with the STS 41-D data and laboratory recombination spectra. No evidence is seen for a second maximum in these last data. However, the NO_2 recombination continuum may take on a different shape, depending on the recombining species and the available internal energy; and on the type of Shuttle surface material and its temperature. It is interesting to note recent laboratory glow results wherein a single maximum at 820 nm in glow signal was seen in an O (0.16 eV energy) + NO + Ni surface experiment [9].

The second striking feature is that the glow signal falls below our present detection limit at an energy of 4 eV, and this represents an upper energy bound to the true threshold. To obtain an estimate of the threshold, we use the following pieces of information: (a) the O + NO (surface) system gains 3.1 eV by the ON-O bond formation, (b) one requires about 0.5 eV to dislodge the electronically-excited NO_2^* from the surface, (c) the NO_2^* leaves the surface with about 1.3 eV kinetic energy, and (d) the maximum internal electronic excitation energy of NO_2^* corresponds to the 400 nm (3.1 eV) onset of the LEO-observed glow. Thus, the center-of-mass threshold energy T_{cm} is given by T_{cm} + (a) = (b) + (c) + (d), or T_{cm} = 1.8 eV, and T_{lab} = 1.8 x (16/10.4) = 2.8 eV (neglecting the small thermal energy of the surface-bonded NO). This is consistent with our upper limit of 4 eV.

As in the O^- case, no identification of the emission continua is possible without understanding the mechanism of the glow process. To this end, work is currently underway to carry out the glow measurements under ultrahigh vacuum conditions, by playing different gases over the solid target surface and identifying which gases, if any, enhance the glow.

Work is also planned to explore the spectral region below 600 nm. While some of this region is obscured by the detaching argon-ion laser lines, wavelengths below 450 nm are accessible.

5   ACKNOWLEDGEMENTS

6   REFERENCES

1. H. B. Garrett, A. Chutjian and S. Gabriel, "Space Vehicle Glow and Its Impact on Spacecraft Systems," J. Spacecraft and Rockets *25*, 321-340 (1988).

2. G.R. Swenson, S.B. Mende, and K.S. Clifton, "Ram Vehicle Glow Spectrum: Implication of NO2 Recombination Continuum," Geophysical Research Letters *12*, 97-100 (1985).

3. L.M. Branscomb, S.J. Smith, and G. Tisone, "Oxygen Metastable Production Through Photodetachment," J. Chem. Phys. *43*, 2906-7 (1965).

4. A. Fontijn, C.B. Meyer, and H.I. Schiff, "Absolute Quantum Yield Measurements of the NO-O Reaction and its use as a Standard for Chemiluminescent Reactions," J. Chem. Phys. *40*, 64 (1964).

5. D.E. Paulson, W.F. Sheridan and R.E. Huffman, "Thermal and Recombination Emission of NO_2," J. Chem. Phys. *53*, 647 (1970).

6. J.-H Yee and A. Dalgarno, "Radiative Lifetime Analysis of the Shuttle Optical Glow," J. Spacecraft and Rockets *23*, 635-40 (1986).

7. O. H. Crawford, "Oscillations in Photodetachment Cross Sections for Negative Ions in Magnetic Fields," Phys. Rev. A *37*, 2432-40 (1988).

8. H. F. Krause, "A Novel High-Resolution Experimental Approach for Studying Laser Photodetachment in a Magnetic Field," Fourth Int. Symp. Prod. and Neutralization of Negative Ion Beams (Brookhaven, N.Y., 27-31 Oct. 1986); and unpublished results (Oak Ridge Nat. Lab., 1989).

9. G.A. Arnold and D.J. Coleman, "Surface Mediated Radical Recombination Luminescence: O + NO + Ni," J. Chem. Phys. *88*, 7147-56 (1988).